Pestic. Sci. 1998, **53**, 300–310

Methods for Determining the Vapour Pressure of Active Ingredients Used in Crop Protection. Part V: Thermogravimetry Combined with Solid Phase MicroExtraction (SPME)‡

Thomas Kröhl,* Roland Kästel, Werner König, Hans Ziegler, Harald Köhle & Adolf Parg

BASF Aktiengesellschaft, Crop Protection Product Development, 67114 Limburgerhof, Germany

6 November 1997; revised version received 24 February 1998; accepted 30 March 1998)

Abstract: The well-established evaporation rate method for determining the vapour pressure of active ingredients in crop protection down to the order of 10^{-12} mbar can be supplemented by the new sample preparation technique of Solid Phase MicroExtraction (SPME). With this technique, it is possible to identify evaporating substances by analysis after partitioning into the polymer coating of a thin fibre in the outlet-gas flow of thermogravimetric equipment.

The active ingredients fenpropimorph, kresoxim-methyl, metolachlor, clomazone and (*Z*)-9-dodecenyl acetate were used in this study, which showed that, despite the relatively small amount of collected material, an analytical identification of the evaporating compound by SPME/GC can be successfully achieved. In particular, the experiments have demonstrated a clear correlation between the linearity of the weight loss curve and the evaporation process of a pure compound.

In the case of organic compounds that are unstable to heat, the SPME method can also be utilized to show whether, and at what temperatures, decomposition of the sample into fragments of higher volatility occurs. For example, the insecticide dimethoate showed a clear temperature dependence of both evaporation behaviour and in the SPME/GC analysis. © 1998 SCI

Pestic. Sci., **53**, 300–310 (1998)

Key words: vapour pressure; evaporation rate; thermogravimetry; active ingredients in crop protection; solid phase microextraction (SPME); gas chromatography

1 INTRODUCTION

One of the most important physical parameters of active substances in crop protection is their vapour pressure. This parameter belongs to the standard properties of the physicochemical data base for the registration of plant protection products. It is the major auxiliary variable for calculating auxiliary volatility, and thus it is a significant factor for predicting atmospheric concentrations of the substances.

Our method for determining vapour pressure based on measurements of the evaporation rate at different

* To whom correspondence should be addressed.
Email address: thomas.kroehl@apd.x400.basf-ag.de
‡ Part IV: Gückel, W. *et al.*, *Pestic Sci.* **45** (1995) 27–31.

 Pestic. Sci. 0031-613X/98/$17.50. Printed in Great Britain

temperatures at ambient pressure is described in earlier publications.[1–3] Using the newer, thermogravimetric method (TG method), which is a further development of previous procedures, it is now possible to determine vapour pressures of solid and liquid substances as low as 10^{-12} mbar (10^{-10} Pa).[4]

A disadvantage of the existing method is that only an indirect determination of the evaporated compounds is made. The method is based on the assumption that a linear decrease in the weight of the sample during isothermal measurement corresponds to the evaporation of the pure compound. However, a specific analytical determination of the evaporating substances is needed to demonstrate that this assumption is correct.

The well-known gas saturation method[5] uses gas chromatography (GC) or gravimetry as the specific analytical method, depending on the particular sample characteristics. Commercially available equipment for the gas saturation method, such as Netzsch Dampfdruckanalysator VPA 434 work, for example, with a gas chromatograph for analysis. In the apparatus VPA 434, a stream of nitrogen gas is passed over the substance in such a way that it becomes saturated with its vapour and the latter is then collected in a suitable trap (e.g. Tenax). Measurement of the amount of material transported by a known amount of carrier gas is used to calculate the vapour pressure at a given temperature. However, this apparatus is restricted to vapour pressures above 10^{-5} Pa and, therefore, is not suitable for active ingredients with lower volatility.[6]

In recent years, solid phase microextraction (SPME) has developed into a powerful method to prepare samples for chemical analysis. SPME was developed in the late 1980s by J. Pawliszyn and co-workers at the University of Waterloo, Canada, as a new method to prepare samples without using any solvent and with no requirement for sample work-up.[7–10] The main part of an SPME device is a fine fused-silica fibre which is coated with a polymer sorbent that has a high affinity for organic compounds. The SPME procedure consists basically of two steps: (1) extracting analytes by partitioning them between the sample and the coating of the fibre and (2) desorption of enriched analytes into an analytical instrument. In this way, organic compounds can be concentrated from very dilute aqueous or gaseous samples without using any solvent.[11]

Applications of SPME most commonly reported in the chemical literature include the analysis of environmental water or air samples,[12] the determination of pesticides,[13,14] soil analysis,[15,16] and many further examples in the food, pharmaceutical and toxicological fields. Analysis of pesticides is reported almost exclusively for aqueous samples, whereas the detection of volatile compounds in the vapour phase is relatively rare. An interesting example of analysis in biology has been shown for airborne pheromones, where SPME was used to analyse volatiles emitted by living insects.[17]

This paper describes an analytical determination of evaporated chemicals using a combination of our established TG method with the SPME technique for sample preparation and gas chromatography as standard analytical method.

2 MATERIALS AND METHODS

2.1 Materials

Fenpropimorph (**1**), kresoxim-methyl (**2**), metolachlor (**3**), clomazone (**4**), (*Z*)-9-dodecenyl acetate (**5**) and dimethoate (**6**) analytical standards were used for the experiments in this study (Fig. 1). These are the active ingredients of the commercial products 'Corbel'™, 'Discus'™, 'Pyracur'™, 'Command'™, 'Rak 1 Plus'™ and 'Perfekthion'™, respectively. The properties of the active ingredients are presented in Table 1. Methanol and acetone (p.a.) were used as solvents for method development.

2.2 SPME device

The SPME device (Supelco, Deisenhofen, Germany) used in this study is shown in Fig. 2. The sorbent for

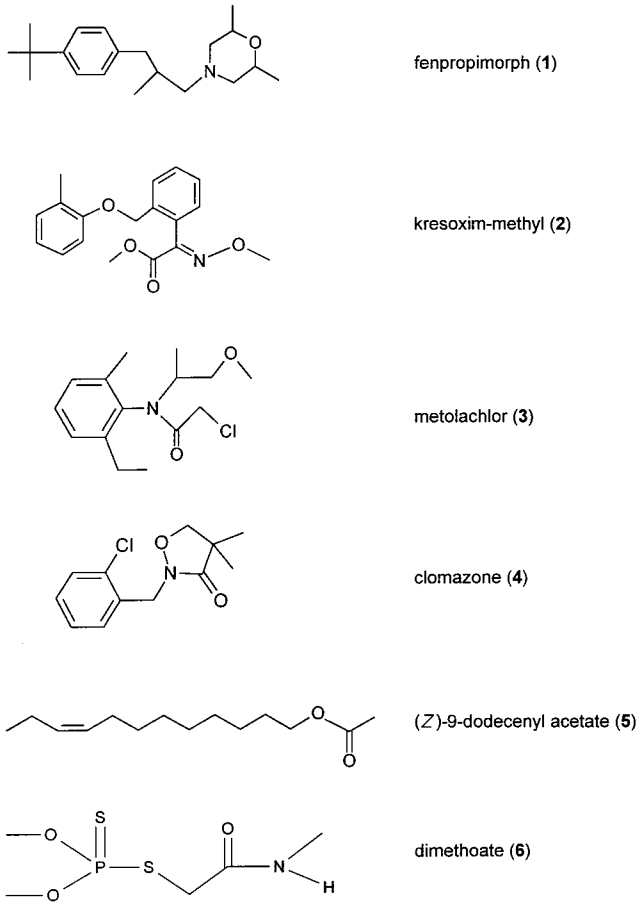

Fig. 1. Active substances used in this study.

TABLE 1
Properties of Active Ingredients Used in this Study

Active ingredient	*Purity* (%)	*Rel. mol. mass*	*m.p.*[a] (°C)	*Vapour pressure at 20°C (mbar)*[b]
Fenpropimorph (**1**)	99·6	303·5	Oil	$2{\cdot}20 \times 10^{-5}$
Kresoxim-methyl (**2**)	99·7	313·4	100	$2{\cdot}30 \times 10^{-8}$
Metolachlor (**3**)	98·1	283·8	Oil	$1{\cdot}70 \times 10^{-5}$
Clomazone (**4**)	99·7	239·7	Oil	$1{\cdot}92 \times 10^{-4}$
(*Z*)-9-Dodecenyl acetate (**5**)	93·5	226·4	Oil	$6{\cdot}50 \times 10^{-4}$
Dimethoate (**6**)	99·8	229·3	45	$2{\cdot}90 \times 10^{-6}$

[a] m.p. = melting point, determined by DSC (differential scanning calorimetry).
[b] 1 mbar = 100 Pa.

extracting the analytes from aqueous or gas phases is coated onto a fused-silica fibre that acts as a carrier rod. The fibre is connected to a stainless steel tube to increase the mechanical strength. A specially designed syringe is used for taking up the stainless steel rod by withdrawing it into the syringe needle. The syringe makes the device portable and allows, for example, for an easy accommodation in a gas chromatograph injector.

A variety of sorbent materials can be used for SPME of different groups of analytes. The most successful stationary phase is polydimethylsiloxane (PDMS), which is available in thicknesses of 7, 30 and 100 μm and is especially suitable for non-polar compounds. Polyacrylate and carbowax are used for polar compounds, whereas polyimide coatings extract chlorinated hydrocarbons.

For all the active ingredients (see Table 1) in this study, non-polar PDMS-coated fibres were used.

To extract analytes from their matrix, the fibre has to be pushed out of the needle by pressing down the plunger (Fig. 2). After an appropriate time of exposure of the coating to the sample, the fibre is completely

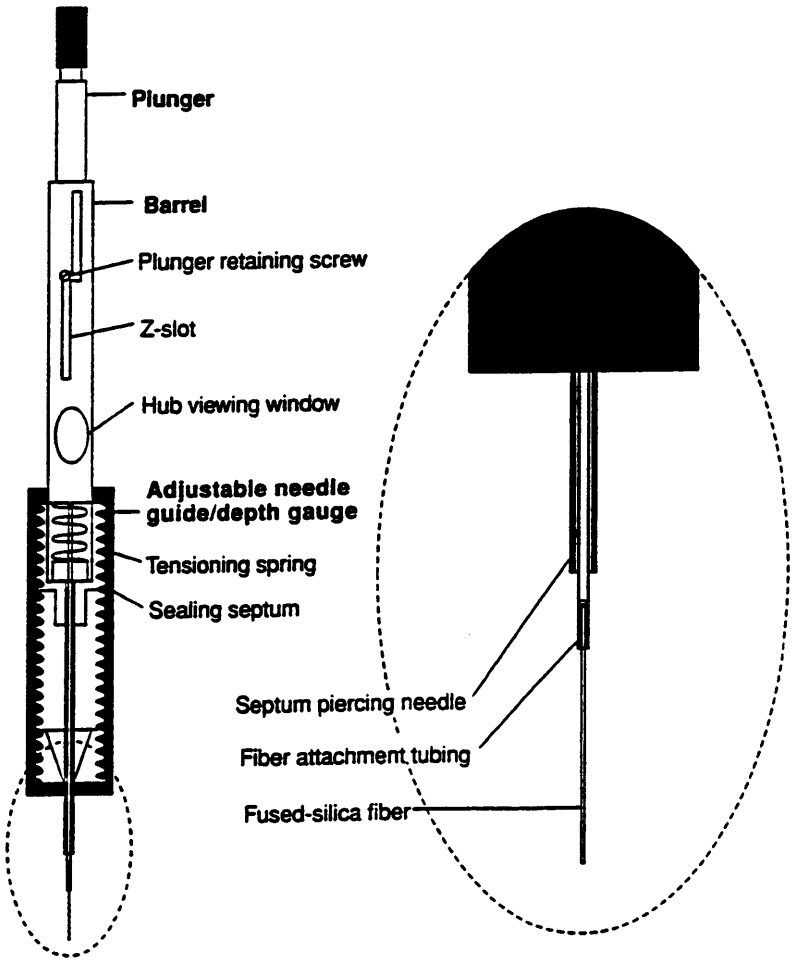

Fig. 2. Schematic diagram of a SPME device (from Ref. 11).

TABLE 2
Chromatographic Conditions Used in this Study

Parameter	*Condition*	*Active ingredient (cf. Table 1)*
GC	HP 5890	**1**
	Varian 3600	**2–6**
Column	CP-Sil-5 CB, Length 25 m, Diam. 0·32 mm	**1**
	HP 5, Length 30 m, Diam. 0·32 mm	**2–6**
Carrier gas	N_2, 30 ml min^{-1}	**1**
	H_2, 30 ml min^{-1}	**1–6**
	He, 1 bar	**2–6**
	Syn. air, 300 ml min^{-1}	**1–6**
Detector	FID	**1–6**
Injector temp.	240°C	**1**
	280°C	**2–6**
Detector temp.	280°C	**1–6**
Oven temp.	100°C 3 min, 40°C min^{-1}, 250°C 5 min	**1**
	200°C	**2**
	60°C 3 min, 30°C min^{-1}, 220°C 5.7 min	**3, 4**
	60°C 3 min, 30°C min^{-1}, 220°C 3.7 min	**5**
	60°C 3 min, 30°C min^{-1}, 150°C 14 min	**6**
Split	1 : 5	**1**
	1 : 4	**2–6**
Film coating thickness	7 μm PDMS[a]	**2–6**
	30 μm PDMS	**2–5**
	100 μm PDMS	**1–4**

[a] PDMS = polydimethylsiloxane.

withdrawn into the needle and immediately transferred to a gas chromatograph, where the analytes are thermally desorbed from the fibre coating in the heated injector port for analysis. Further technical details and the theoretical background of SPME are broadly described in the literature.[9,11]

2.3 Gas chromatography

HP 5890 or Varian 3600 gas chromatographs were used for analysis. Existing GC methods for the active ingredients in Fig. 1 were evaluated and modified to give satisfactory chromatographic results. The chromatographic conditions used in this study are shown in Table 2.

Typical chromatograms of compound **1** are presented in Fig. 3. For each preparation the retention time of 6·75 min was found to be reproducible. The retention times for all compounds investigated are listed in Table 3.

2.4 Combining evaporation rate measurements with SPME

A schematic diagram of the device used to determine evaporation rates is shown in Fig. 4.[4] The sample carrier plate, hanging on a microbalance in a thermoregulated casing, is swept by a stream of dry nitrogen gas which carries the vaporized molecules. The evapo-

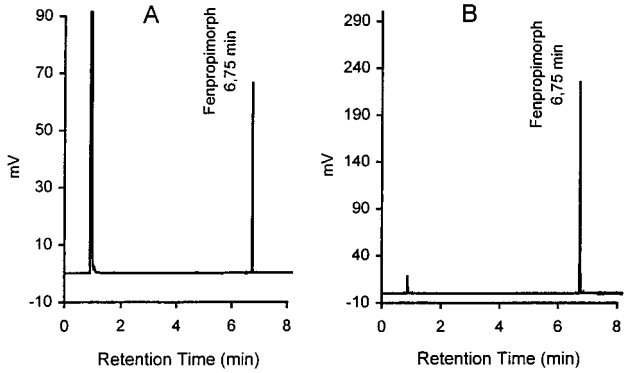

Fig. 3. GC chromatograms for compound **1**, obtained under conditions described in Table 2. (A) Acetonic solution of **1** (45.2 mg $litre^{-1}$); (B) Aqueous solution of **1** (124.0 mg $litre^{-1}$).

TABLE 3
GC Retention Times for Compounds Investigated

Active ingredient	*Retention time[a] (min)*
Fenpropimorph (**1**)	6·75
Kresoxim-methyl (**2**)	10·67
Metolachlor (**3**)	11·05
Clomazone (**4**)	9·57
(*Z*)-9-Dodecenyl acetate (**5**)	8·57
Dimethoate (**6**)	16·4

[a] Determined with standard solutions in acetone (1 g $litre^{-1}$).

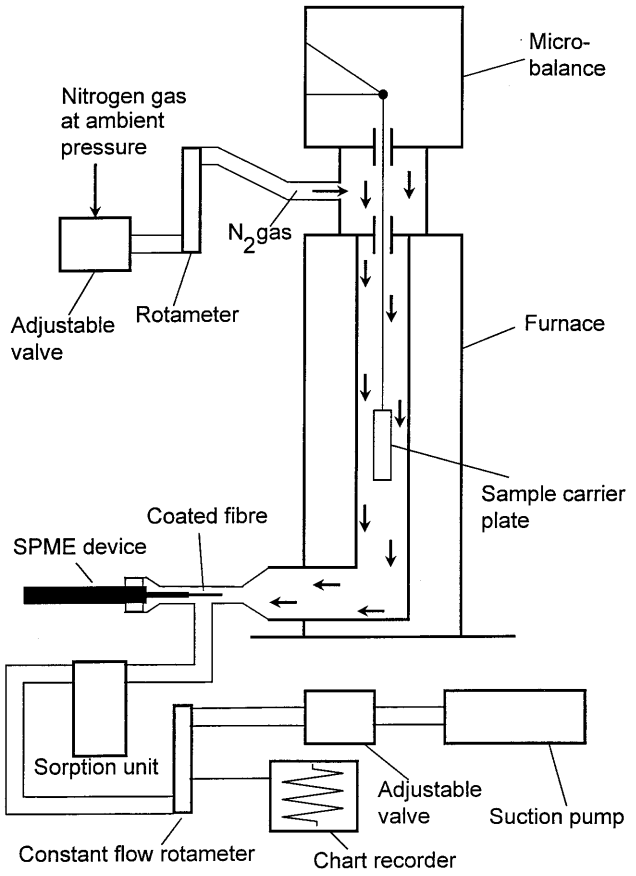

Fig. 4. Schematic diagram of the apparatus used to determine the evaporation rates of active ingredients, combined with an SPME device.

ration rate v at a definite temperature is calculated from the weight loss Δm of the sample plate by

$$v = \frac{\Delta m}{Ft} \text{ (g cm}^{-2}\text{ h}^{-1}\text{)},$$

where F = surface area of the sample plate (cm^2), and t = time (h) for a weight loss Δm (g).

A sorption unit prevents environmental pollution. In order to identify the evaporating material, a small proportion of it is collected between the furnace and the sorption unit for subsequent analysis. As shown in Fig. 4, a SPME device is installed for this purpose directly at the outlet of the thermogravimetric furnace. The SPME is held by a fixed adapter with an inner thread into which the syringe can be screwed.

3 RESULTS AND DISCUSSION

3.1 Extraction from a saturated vapour phase

Extraction of compounds from their own saturated vapour phase was carried out in 10-ml ampoules, closed with a septum, where a small amount of the substance was deposited on the bottom of the ampoule. After piercing the septum with the SPME needle, the coated fibre was exposed to the sample vapour and absorption into the coating took place.

3.1.1 Dependence on extraction time

Figure 5 shows a SPME/GC chromatogram for fenpropimorph (**1**), extracted with a 100-µm PDMS fibre with an extraction time of 5 h. The peak of the compound appears sharply at the same retention time as in the chromatograms of Fig. 3. The dependence of the peak area on the extraction time is shown in Fig. 6. The peak area increases linearly with time. This illustrates that, as a consequence of the low vapour pressure of the compound at room temperature (Table 1), the equilibrium between the sample fraction dissolved in the siloxane phase and that remaining in the sample bulk has not yet been reached. The coated fibre acts as a sink, absorbing successively all molecules of the slowly evaporating analyte present in the vapour phase.

3.1.2 Different fibres with the same coating thickness

In order to determine the reproducibility between fibres, the absorption behaviour of three different fibres with the same coating thickness (100 µm PDMS) and with the same active ingredient (**1**) was investigated. Results of measurements for six extraction times between 10 and 60 min are presented in Fig. 7. Although the peak area at each point of time differed in the order of $\pm 10\%$, the rates of absorption for each of the three fibres investigated were in good agreement, i.e. repeatable.

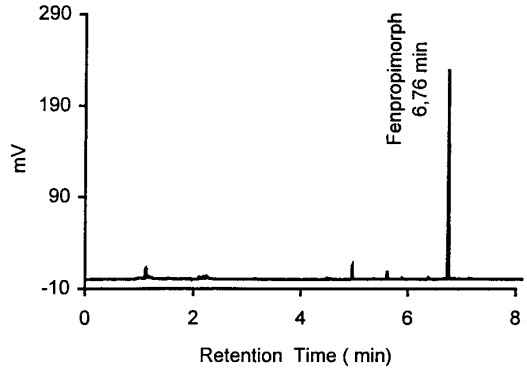

Fig. 5. SPME/GC chromatogram for substance **1**, extracted with a PDMS fibre (100 µm) at room temperature with an extraction time of 5 h.

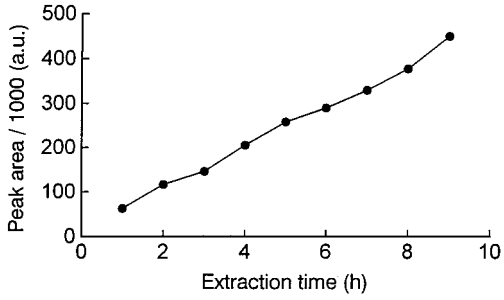

Fig. 6. Dependence of the SPME/GC peak area on the extraction time for the extraction of fenpropimorph (**1**) from its own vapour phase at room temperature.

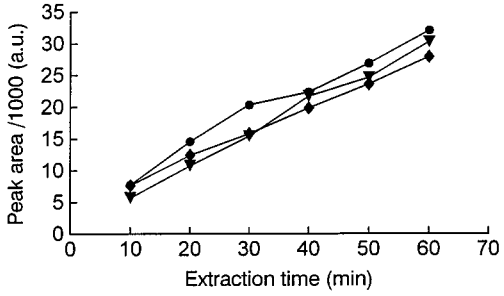

Fig. 7. Dependence of the SPME/GC peak area on the extraction time for fenpropimorph (**1**), extracted at room temperature with three different fibres with the same coating thickness (100 µm PDMS).

3.1.3 Different thicknesses of the fibre coating

Metolachlor (**3**) and clomazone (**4**) were extracted from their vapour phase in 10 ml ampoules at 60°C by placing the ampoules together with the inserted SPME device in a heating chamber. The higher temperature was used to maintain more molecules in the gaseous phase and therefore more vaporized material for collection by the fibre in an appropriate time. Results for an extraction time of 1 h and fibre coating thicknesses of 7, 30 and 100 µm are shown in Fig. 8. Metolachlor (A) could be detected very well with all three fibre thicknesses, more material being taken up by thicker fibre coatings. In the case of clomazone (B), an increase in peak broadening with coating thickness was observed whereby only the 7- and 30-µm fibres were suitable for extraction. The release of analyte molecules from the 100-µm fibre was delayed and an unacceptably broad GC peak was obtained. Obviously, the solubility of clomazone in the coating material is higher than that of metolachlor and the desorption of clomazone is thus more delayed.

3.2 Extraction at the outlet of the thermogravimetric system

3.2.1 Thermally stable compounds

Fenpropimorph (**1**) was used in the first experiments where evaporation rate determinations had been combined with SPME extraction. The results of measurements with an extraction time of 1 h at oven temperatures of 80 and 100°C are presented in Tables 4 and 5. After calibration with standard solutions in acetone, the peak areas were converted to extracted

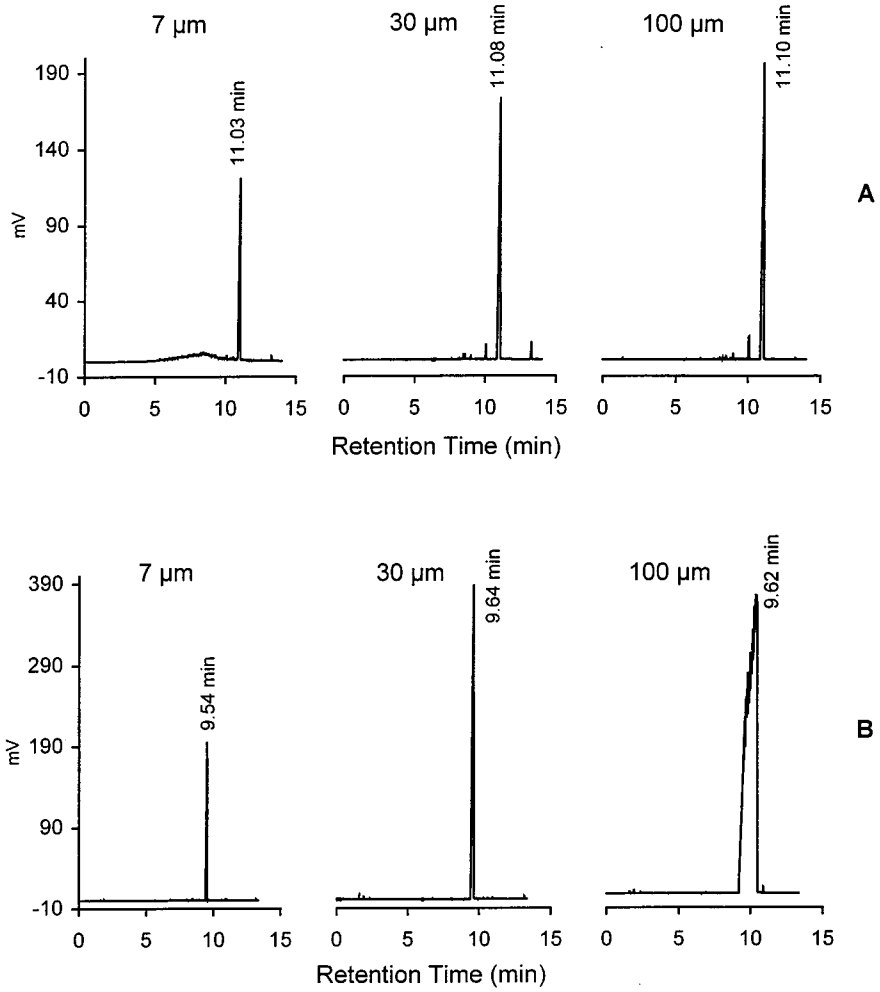

Fig. 8. SPME/GC chromatograms obtained for (A) metolachlor (**3**) and (B) clomazone (**4**), extracted from their vapour phases for 1 h at 60°C with three different fibre coating thicknesses (7, 30 and 100 µm).

TABLE 4
SPME/GC Results with Fenpropimorph (**1**) at 80°C.

	Evaporated mass M_{eva} (*mg*)	*GC peak area*	*SPME-extrac. mass* M_{ext} (*ng*)	M_{eva}/M_{ext}
	0·88	342 641	1435·8	613
	0·88	346 847	1453·4	605
	0·86	353 800	1482·6	580
	0·82	349 140	1463·1	560
	0·91	382 494	1602·8	568
	0·92	355 571	1490·0	617
Mean value	0·88	355 082	1488·0	591
Rel. standard deviation (%)	4·10	4·01	4·01	4·14

amounts in nanograms (ng). Although the absorbed amounts are not very high, their standard deviations are relatively small, indicating a good repeatability of the measurements. An increase of the furnace temperature from 80 to 100°C increased the amount of absorbed material by a factor of about three. The last columns of Tables 4 and 5 show the ratio between the evaporated mass and the SPME-extracted mass. This

TABLE 5
SPME/GC Results with Fenpropimorph (**1**) at 100°C.

	Evaporated mass M_{eva} (*mg*)	*GC peak area*	*SPME-extract. mass* M_{ext} (*ng*)	M_{eva}/M_{ext}
	3·42	1 228 471	5147·8	664
	3·28	1 104 116	4626·7	709
	3·56	1 196 112	5012·2	710
	3·52	1 136 832	4763·8	739
	3·49	1 159 088	4857·1	719
	3·28	1 109 079	4647·5	706
Mean value	3·43	1 155 616	4842·5	708
Rel. standard deviation (%)	3·54	4·26	4·26	3·45

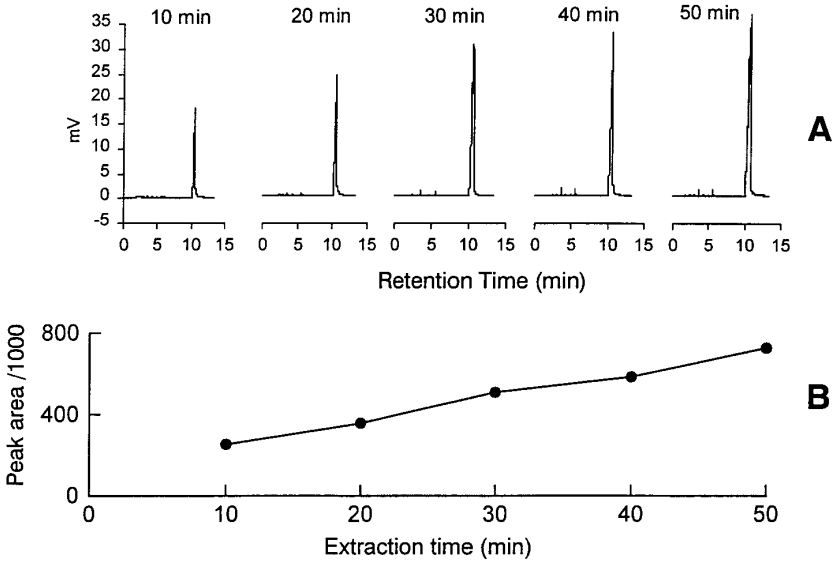

Fig. 9. (A) SPME/GC chromatograms obtained for kresoxim-methyl (**2**) with extraction times of 10–50 min and (B) the calculated peak areas; furnace temperature during evaporation: 120°C.

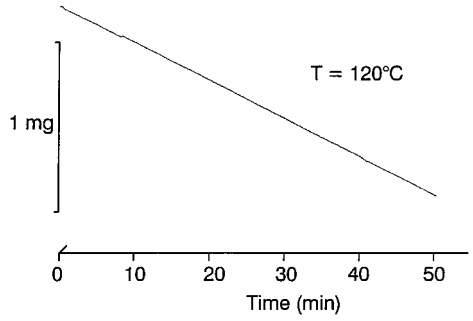

Fig. 10. Weight loss of the test sample kresoxim-methyl (2) during evaporation for 50 min at a furnace temperature of 120°C.

ratio is very large, which indicates that most of the evaporated material is passing the SPME device at a distance at which it cannot be absorbed by the coating. Nevertheless, the amount of extracted analyte is still sufficiently high to identify the evaporated substance by SPME analysis.

Kresoxim-methyl (**2**), a fungicide with a relatively low vapour pressure (Table 1), had to be extracted at higher temperatures. Results for a furnace temperature of 120°C are shown in Fig. 9, where the absorbed amount is plotted as a function of the extraction time. As with fenpropimorph (Fig. 6), the absorbed amount increased linearly with time, which indicates that the absorbing capacity of the fibre coating was not exceeded (Fig. 9B).

The GC chromatograms in Fig. 9A show the peak of the prepared test substance only; there are no further peaks to indicate impurities, contaminants or decomposition products. The weight of the sample, measured during the evaporation process, decreased linearly with time (Fig. 10). Thus, a linear decreasing weight-loss curve corresponds to the evaporation of a pure compound.

Experimental data obtained with metolachlor (**3**), clomazone (**4**) and (*Z*)-9-dodecenyl acetate (**5**) are shown in Fig. 11. SPME extractions were carried out with a 30-μm fibre at a furnace temperature of 80°C and an extraction time of 1 h (compounds **3** and **4**). The more volatile (*Z*)-9-dodecenyl acetate (**5**) was extracted for 30 min at 40°C.

All these active ingredients displayed linear evaporation behaviour (Fig. 11A), and SPME/GC analysis detected only the pure ingredients, indicated by sharp main GC peaks (Fig. 11B).

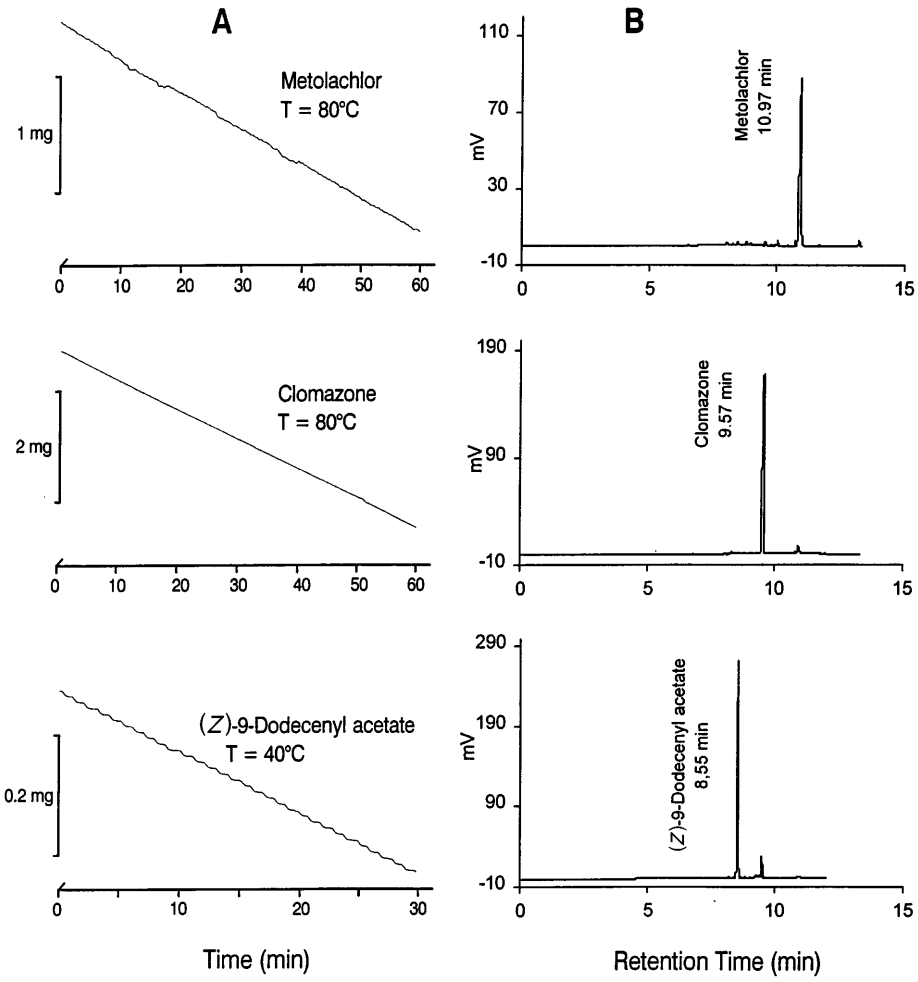

Fig. 11. (A) Weight loss curves and (B) SPME/GC chromatograms for metolachlor (**3**), clomazone (**4**) and *Z*9-dodecenylacetate (**5**). The substances (**3**) and (**4**) were extracted for 1 h with a 30-μm fibre at a furnace temperature of 80°C, and (**5**) for 30 min at 40°C.

3.2.2 *Thermally unstable compounds*

The determination of the vapour pressures of low-volatility, thermally unstable compounds is rendered more difficult because the measurements have to be performed at lower temperatures to avoid thermal decomposition of the substances. Low temperatures lead to relatively slow weight losses of the sample and thus the measurements are, in some cases, near the resolution limit of the thermogravimetric system. For this type of investigation, SPME analysis can help to determine whether decomposition of the compound has occurred.

The insecticide dimethoate (**6**) was chosen as a relatively low-volatility ingredient which shows instability at elevated temperatures (Fig. 12).

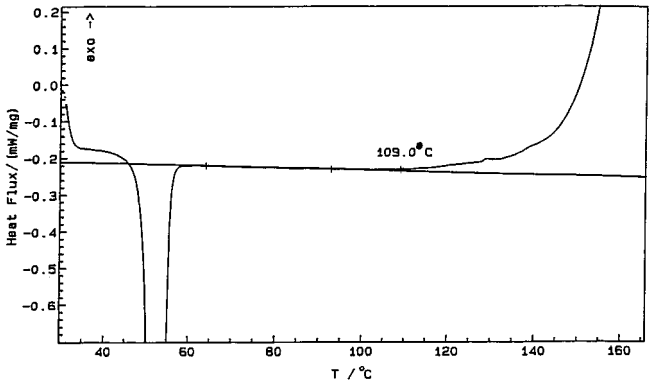

Fig. 12. Differential scanning calorimetry (DSC) diagram for dimethoate (99.8%), $m = 8{\cdot}48$ mg, heating rate 5 K min^{-1}. The onset for decomposition appears at about 110°C.

The results of evaporation experiments carried out at 80, 100, 120 and 140°C, accompanied by SPME/GC analysis (7-μm PDMS fibre) are presented in Fig. 13. The SPME/GC diagram for 80°C (Fig. 13A, left) shows the peak of only dimethoate at a retention time of above 16 min. There are no peaks from decomposition products. This corresponds to the linear shape of the weight loss curve (Fig. 13A, right). Also at 100°C (Fig. 13B) the GC chromatogram shows no decomposition products and the weight loss curve remained linear, which indicates that the studied compound had not yet begun to decompose.

Increasing the temperature by another 20°C to 120°C (Fig. 13C), caused additional peaks to appear in the GC

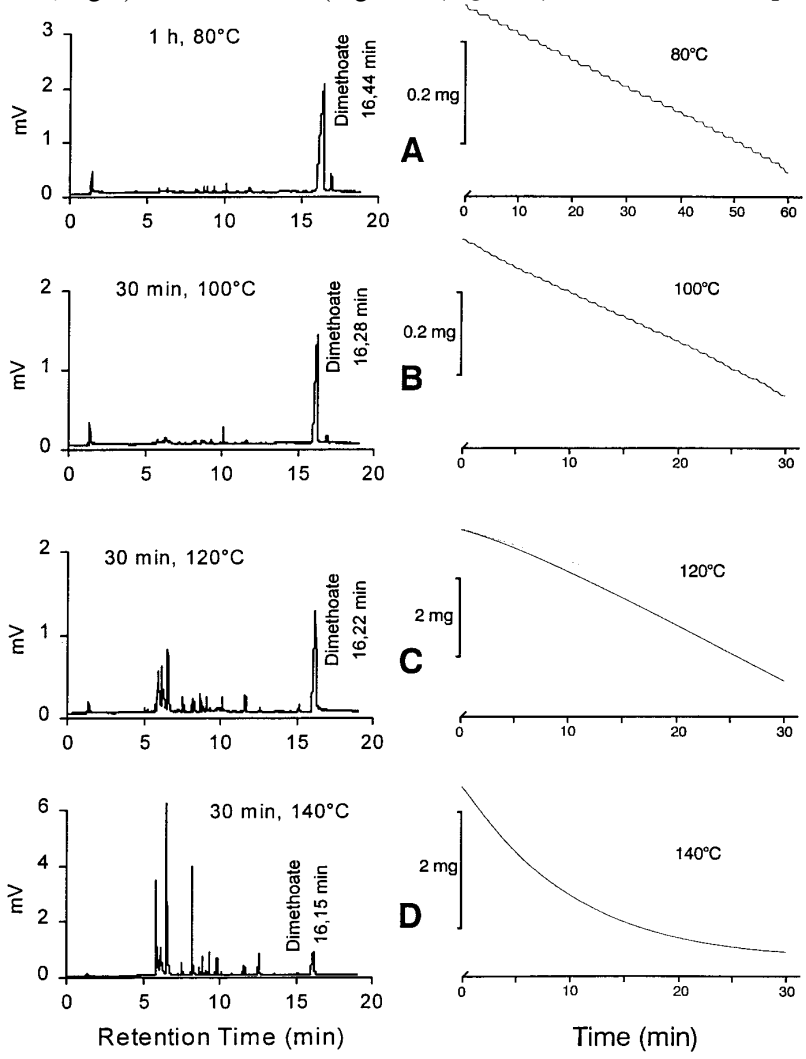

Fig. 13. GC chromatograms (left) and weight loss curves (right) from evaporation experiments with dimethoate (**6**) at (A) 80°C, (B) 100°C, (C) 120°C and (D) 140°C.

chromatogram, mainly at shorter retention times between 5 and 10 min. Together with the downwards inflection of the weight loss curve, this is a clear evidence that the compound had started to decompose into smaller fragments of higher volatility.

Finally, at 140°C (Fig. 13D), only a small peak of intact dimethoate could be observed, while the fragment peaks dominate the chromatogram. The decreasing slope of the weight loss curve resulted from an increasing encrustation of the sample on the glass plate as a consequence of the decomposition of the compound, and thus to a decreasing evaporation rate of the material with time.

Like Tables 4 and 5, Table 6 presents a summary of evaporation/SPME/GC experiments for all compounds investigated. The results demonstrate the following: 1. As with fenpropimorph (Tables 4 & 5), only a relatively small percentage of the evaporated matter is collected by the SPME device at the outlet of the thermogravimetric system 2. Because of the differences in the chemical structure and in the polarity of the compounds investigated, each has a different affinity to the fibre-coating material, as indicated by the different values for the ratio of evaporated mass to SPME-extracted mass.

4 CONCLUSIONS

The thermogravimetric method to determine the vapour pressure of organic compounds has been combined with the new technique of solid phase microextraction (SPME). This technique, initially developed as a solvent-free method to extract organic compounds from aqueous samples, can also be used to extract both volatile and semi-volatile substances from the vapour phase.

SPME extractions from saturated vapour phases were carried out in septum-closed ampoules with three different active ingredients. In experiments designed to establish the dependence of the SPME/GC signal on the extraction time it could be shown that, as a consequence of the low evaporation rates, an equilibrium between the extracted amount and the sample in its matrix could not be reached within an appropriate time. The GC peak areas increased linearly with the extraction time, which indicates that each molecule of the slowly evaporating substance was successively absorbed by the fibre coating. This would appear to indicate that this kind of 'non-equilibrium'-state is a typical characteristic of extractions from vapour phases. As reported in the literature, this is different from SPME extractions from aqueous matrices, where a steady state is reached within a relatively short period of time (mostly <1 min).[10]

The thickness of the fibre coating is an experimental parameter whose relevance differs, depending on the solubility of the analyte in the coating material or its affinity to the latter. Generally, a widening of the GC peak was observed with an increase in coating thickness, such that, in some cases (e.g. clomazone), only thinly coated fibres could be used for acceptable GC results.

Installing a SPME device at the outlet of a thermogravimetric apparatus makes it possible to collect a small proportion of the volatiles for subsequent GC analysis. It could be shown for several thermally stable compounds that, despite the relatively small percentage of collected material, an analytical identification of the evaporating compound by SPME/GC could be successfully achieved. In particular, the experiments have

TABLE 6
Evaporation/SPME/GC-Results for Compounds **1**–**6**

Active ingredient	*Temp.* (°C)	*Time*[a] (*h*)	M_{eva} [b] (*mg*)	M_{ext} [c] (*ng*)	M_{eva}/M_{ext}
Fenpropimorph (**1**)	80	1	0·88	1488	591[d]
	100	1	3·43	4843	708[e]
Kresoxim-methyl (**2**)	120	1	1·726	7775	222
Metolachlor (**3**)	80	1	0·887	1243	714
	100	1	3·515	4162	845
Clomazone (**4**)	60	1	0·678	425	1595
	80	1	2·96	2627	1127
(*Z*)-9-Dodecenyl acetate (**5**)	30	0·5	0·089	430	206
	40	0·5	0·21	3056	69
Dimethoate (**6**)	80	1	0·33	106	3113
	100	1	0·75	117	6410

[a] Time = evaporation time in the thermogravimetric system = SPME-extraction time.
[b] M_{eva} = evaporated mass in the thermogravimetric system.
[c] M_{ext} = SPME-extracted mass at the outlet of the thermogravimetric system.
[d] From Table 4.
[e] From Table 5.

demonstrated a clear correlation between the linearity of the weight-loss curve and the evaporation process of a pure compound.

In the case of organic compounds that are unstable to heat, the SPME/GC method could be utilized to show whether, and at what temperatures, a decomposition of the compound into fragments of higher volatility occurred. For example, the insecticide dimethoate exhibited both a linear evaporation behaviour and a single GC peak at temperatures up to approximately 100°C, whereas at temperatures of 120°C and higher, fragments from decomposition processes dominated the GC chromatograms.

In conclusion, evaporation rate measurements can be carried out with a greater degree of certainty concerning the identity of the evaporating substances, when combined with the SPME/GC technique. Using mass spectral detection in place of FID could provide even more information regarding the chemical identity of the vaporized species. Experiments along these lines and also those using a combination of SPME and HPLC, especially for weakly volatile or thermally labile compounds, are in progress.

ACKNOWLEDGEMENTS

We thank Mr Anton Hörner, Mr Günter Walter, Mr Markus Keller, Mr Bernd Machauer, Mr Michael Siebecker, Mr Ralf Kreucher and Mr Andreas Bog for excellent technical assistance and for data evaluation.

REFERENCES

1. Gückel, W., Synnatschke, G. & Ritttig, R., A method for determining the volatility of active ingredients used in plant protection. *Pestic. Sci.*, **4** (1973) 137–47.
2. Gückel, W., Synnatschke, G. & Ritttig, R., A method for determining the volatility of active ingredients used in plant protection II. Applications to formulated products. *Pestic. Sci.*, **5** (1974) 393–400.
3. Gückel, W., Kästel, R., Lewerenz, J. & Synnatschke, G., A method for determining the volatility of active ingredients used in plant protection Part III: The temperature relationship between vapour pressure and evaporation rate. *Pestic. Sci.*, **13** (1982) 161–8.
4. Gückel, W., Kästel, R., Kröhl, T. & Parg, A., Methods for determining the vapour pressure of active ingredients used in crop protection. Part IV: An improved thermogravimetric determination based on evaporation rate. *Pestic. Sci.*, **45** (1995) 27–31.
5. EPA Product Properties Test Guideline OPPTS 830.7950 Vapor Pressure, EPA 712-C-95-043 (1995).
6. Netzsch Dampfdruckbestimmung VPA 434, Technische Daten (1997).
7. Berlardi, R. & Pawliszyn, J., The application of chemically modified fused silica fibers in the extraction of organics from water matrix samples and their rapid transfer to capillary columns. *Water Pollution Research J. of Canada*, **24** (1989) 179.
8. Arthur, C. & Pawliszyn, J., Solid phase microextraction with thermal desorption using fused silica optic fibers. *Anal. Chem.*, **62** (1990) 2145–8.
9. Arthur, C., Potter, D., Buchholz, K., Motlagh, S. & Pawliszyn, J., Solid phase microextraction for the direct analysis of water: Theory and practice. *LC-GC*, **10** (1992) 656–61.
10. Louch, D., Mortlaugh, S. & Pawliszyn, J., Dynamics of organic compounds extraction from water using liquid-coated fused silica fibers. *Anal. Chem.*, **64** (1992) 1187–99.
11. Zhang, Z., Yang, M. & Pawliszyn, J., Solid phase microextraction. *Anal. Chem.*, **66** (1994) 844–53.
12. Chai, M., Arthur, C., Pawliszyn, J., Berlardi, R. & Pratt, K., Determination of volatile chlorinated hydrocarbons in air and water with solid-phase microextraction. *Analyst*, **118** (1993) 1501–5.
13. Boyd-Boland, A. & Pawliszyn, J., Solid phase microextraction of nitrogen-containing herbicides. *J. Chromatogr.*, **704** (1994) 163–72.
14. Eisert, R. & Levsen, K., Determination of pesticides in aqueous environmental samples *via* SPME (solid-phase microextraction). *GIT Fachz. Lab.*, **39**(1) (1995) 25–6.
15. Popp, P., Kalibitz, K. & Opperman, G., Application of solid-phase microextraction and gas chromatography with electron-capture and mass spectrometric detection for the determination of hexachlorocyclohexanes in soil solutions. *J. Chromatogr.*, **687** (1994) 133–40.
16. Bengsson, S. & Berglof, T., *Extraction of Pesticides by Solid Phase Microextraction (from Soil)*. Dept. Of Environmental Assessment, Swedish University of Agricultural Sciences, PO Box 7050, Uppsala, Sweden.
17. Malosse, C., Ramirez-Lucas, P., Rochat, D. & Morin, J.-P., Solid-phase microextraction, an alternative method for the study of airborne Insect pheromones (*Metamasius hemipterus*, Coleoptera, Curculionidae). *J. High Resol. Chromatogr.*, **18** (1995) 669–70.